Archives of Materials Science and Engineering

Volume 52
Issue 1
November 2011
Pages 18-22

International Scientific Journal
published monthly by the
World Academy of Materials
and Manufacturing Engineering

Supramolecular complexes C<18-crown-ether-6> and their application in devices for energy generation, storage and transformation

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Received 19.08.2011; published in revised form 01.11.2011

ABSTRACT

Purpose: Formation of supramolecular complexes C<18-crown-ether-6> and investigation of their electrochemical characteristics was the aim of this paper. An organic receptor is inserted in nano/mesopores of activated carbon of these supramolecular complexes.

Design/methodology/approach: Electrochemical studies of supramolecular complexes C<18-crown-ether-6> were carried out by means of impedance spectroscopy, cyclic voltammetry and galvanostatic cycling.

Findings: It is shown that Faraday generation of energy occurs at low positive potentials whereas the capacitive storage – at higher potentials. As result the value of specific capacitance for AC of faradaic process 10000 F/g was reached as well as 154 F/g of non-faradaic process, whereas the same parameters for BAC equal 13350 F/g and 80 F/g, respectively.

Research limitations/implications: This research is a complete and accomplished work.

Practical implications: Supramolecular complexes, obtained in this work, could be regarded as promising electrode materials in devices of energy generation, storage and transformation.

Originality/value: This work is of urgent importance for physics and chemistry of energy generation, storage and transformation, because it opens new possibilities to new highly effective electrode materials search and enables to reach a high values of functional characteristics.

Keywords: Nanoporous carbon; 18-crown-ether-6; Ionistor; Faradaic process

Reference to this paper should be given in the following way:

B.Ya. Venhryn, Z.A. Stotsko, I.I. Grygorchak, S.I. Mudry, O.V. Balaban, Supramolecular complexes C<18-crown-ether-6> and their application in devices for energy generation, storage and transformation, Archives of Materials Science and Engineering 52/1 (2011) 18-22.

PROPERTIES

1. Introduction

Up-date rapid development of electric car construction and non-traditional energetic impressive success of nanoelectronics and spintronics with essential importance selected the deep problems, which lie in the base of principal contradictions between growing requirements of advanced scheme technical solutions and abilities of modern technologies of autonomous devices for generation, transformation and accumulation of energy. Main electrochemical systems, which exist today in above mentioned branch of technology have been developed more than one hundred years ago. On that reason the progress which was reached is considered as elements of supercapacitor technology (1953 year) and energy sources with lithium anode (1959 year). Supercapacitors (ionistors), whose principle of operation is based on polarization of volume charge of electric double layer at the boundary between blocking electrode with electrolyte, have a calling to maintain the high specific power and cyclic characteristics. But, the specific values of energy capacitance of such devices are limited by low value of differential capacitance (~ 25 μF/cm^2), which is notably less than similar parameter of chemical accumulators [1]. The attempts to increase this parameter allowed in seventies of last century to development of new direction in technology of energy storage – creation of so named configuration-hybrid (nonsymmetrical) supercapacitors [2] and functional–hybrid redox- (or pseudo) ionistors [3]. Unfortunately the success, reached in this field not yet as considerable as was expected. Systems, which have been proposed consist of harmful elements (Pb, Cd) [4], besides they are very rare and very expensive (RuO_2) [2, 5]. Isolated attempts to develop the theory as well as experimental studies up till now give no clear understanding how to solve the above mentioned problems. This work has the aim to make one of first steps to solve those problems.

2. Conceptual states and experimental

Analysis of functioning features of above considered devices allows revealing the deficiencies, which determine the low effectiveness of their work. If we know and understand them, we can choose the methods to avoid these problems. We hope that supramolecular compounds are just such the materials, which have many abilities to solve them.

Supramolecular chemistry is the chemistry of molecular ensembles and intermolecular bonds, chemistry beyond the molecules, whose base is interaction of components of host–guest kind with lock–key mean of interaction [6].

This science is comparatively young but due to large number of supramolecular compounds, variety of their properties it joined in itself the informative regions of organic, coordination, physical chemistry, biology and material science. On that reason it transforms into powerful instrument for solving of lot a problems of present-day medicine, physics, instrument-making industry, information technologies with colossal potential for creating of desired materials as well of their properties. In particular, crown-ethers, which link alkaline metals by means "lock-key", can be used as such compounds. In order to stabilize the electrode material in electrolyte solutions and also for modification of energetic diagram of interface between electrode and electrolyte, we propose to create the supramolecular ensemble oh hierarchical architecture C<18-crown-ether-6> according to which molecules of organic receptor of potassium cations are introduced into nano- and mesopores of activated carbon (Fig. 1).

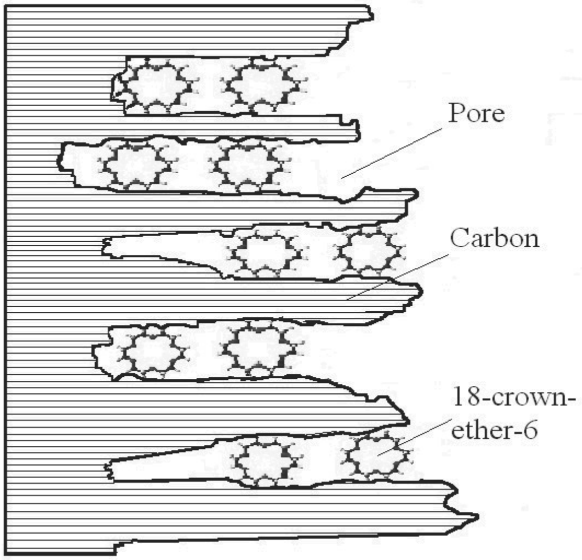

Fig. 1. Supramolecular ensemble C<18-crown-ether 6> of hierarchical architecture according to which molecules of organic receptor of potassium cations introduced into nano- and mesopores of activated carbon

It is well known that activated carbon is the main material for supercapacitors due to its cheapness and blocking properties. In order to determine the influence of developed surface as well as porous structure degree two kinds of activated carbons have been used in experimental investigation. Namely first of them was birch activated carbon (BAC) and another one was carbon, obtained by means of activation carbonization of apricot stones (AC). These materials show the developed surface of different value. Particularly, for BAC it equals 467 m^2/g, whereas this value is of 613 m^2/g for AC. Micropores size of AC and BAC equal 8.7 Å and 10.7 Å, respectively.

Process of 18-crown-ether-6 introducing has been performed at room temperature in vacuum (~ 10^{-2} mm Hg) after preterm desorbtion of activated carbon in vacuum. Particularly, activated carbon was placed in sealed glass vessel and then all this was put in furnace. The thermal annealing in vacuum was carried out during 2 hours at temperature within 130-140°C temperature range. The seepage of saturated solution of 18-crown-ether-6 with C_2H_5OH as solvent, in vacuum for 15 minutes was the final stage of process. Upon thermal seepage in vacuum the flushing of activated carbon with $CH_3CH(OH)CH_3$ and following drainage of material to constant mass was done. Mass increase as well as well as fractal structure change indicated that crown-ether molecules were intercalated into nano- and mesopores of related activated carbon.

Small angle X-ray small angle scattering data were obtained over scattering range 2Θ=0.2-4.0 degree with using the special collimation system both for initial and scattered beams. In order to reduce the parasite scattering from crystal-monochromator, the special slit system was arranged before sample at the distance within 3.5-4.0 cm range. The similar system was installed also before receiving slit of detector that allowed us to reduce the background scattering. Using the LiF perfect crystal and mentioned above the collimation system permitted us to carry the investigation within small angle region, starting from 2Θ=0.2-0.25 degree. The resolution of detector was estimated to be 0.03 degree. The scattered intensities have been measured in transmission regime with step $\Delta 2\Theta$=0.05 degree and exposition 100 s.

An electrochemical studies of obtained supramolecular structure has been carried out in three-electrode cell with chlorine-silver reference electrode. Impedance measurements were done within frequency range (10^{-2}-10^{5} Hz) with using measuring equipment “Autolab” (“Eco Chemie”, Holland), attached software FRA-2 and GPES. Cyclic voltage-current plots of electrochemical cells were recorded with scanning speed of voltage 0.01 V/s. “Charge-discharge” galvanostatic cycles have been maintained by means of electron galvanostatic device.

3. Results and discussion

Results on X-ray small angle scattering shown that upon introducing of crown ether (18-crown-ether-6) the active specific area decreases to 202 and 384 m^2/g respectively. Values of micropore radius were found to be 9.4 Å (C<18-crown-ether-6> on the base of AC) and 9.7 Å (C<18-crown-ether-6> on the base of BAC).

Porous structure of supramolecular complex C<18-crown-ether-6> on the base BAC reveals the fractal type of structure. Fractal aggregates formation of fractal dimension D_s=2.23 occurs (Fig. 2).

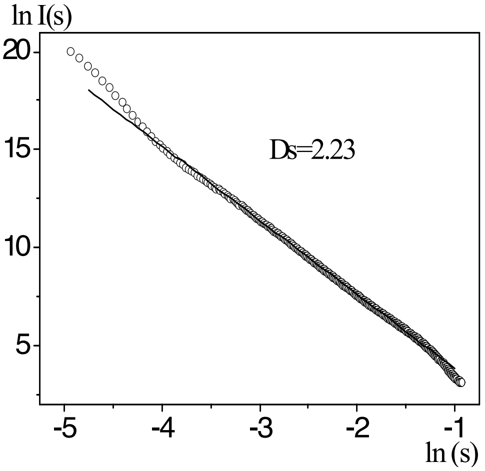

Fig. 2. Scattered intensity versus wave-vector for supramolecular complex C<18-crown-ether-6> on the base BAC

Contrary, analysis of scattered intensity as function of scattering angle for supramolecular complex C<18-crown-ether-6> on the base of AC no reveals the fractal structure formation that results in random distribution of pores (Fig. 3). From this figure follows that dependence of scattered intensity versus wave-vector shows no regions with linear behaviour, indicating absence of fractal structure.

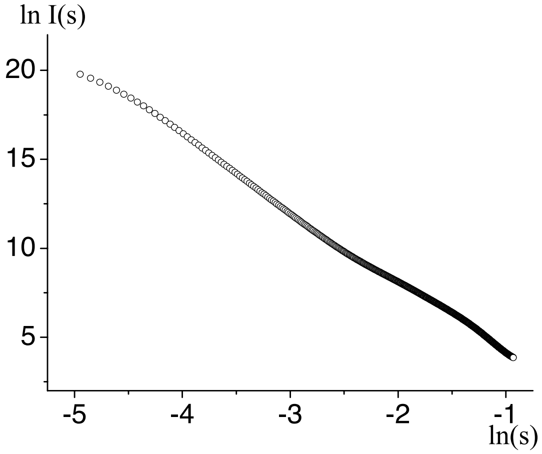

Fig. 3. Scattered intensity versus wave-vector for supramolecular complex C<18-crown-ether-6> on the base AC

“Charge-discharge” galvanostatic cycles for initial BAC and synthesized on its base supramolecular ensemble C<18-crown-ether-6>, from which follows more than twofold decrease of capacitance for last structure are shown in Fig. 4.

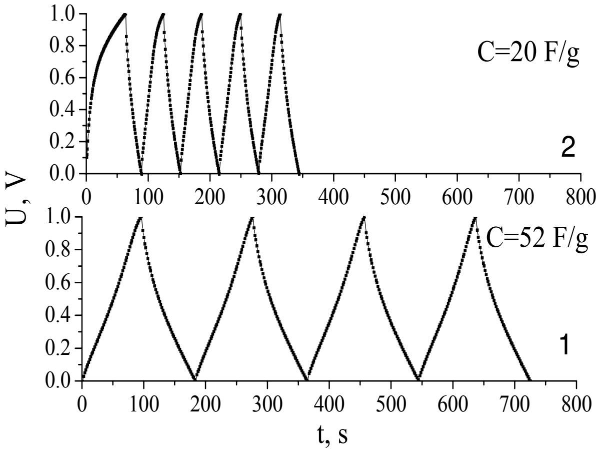

Fig. 4. Galvanostatic “charge-discharge” cycles for initial BAC (1) and for supramolecular complex C<18-crown-ether-6> (2) on its base

In order to clarify the reasons of this effect a farad-volt characteristics within the range of potential -0.5-0.5 V with step 0.1 V have been studied. For each value of applied voltage the Nyquist plots were obtained and computer parametric identification of respective impedance models was performed. The non-ordinary fact was revealed that anode and cathode polarization are remarkably different (Fig. 5).

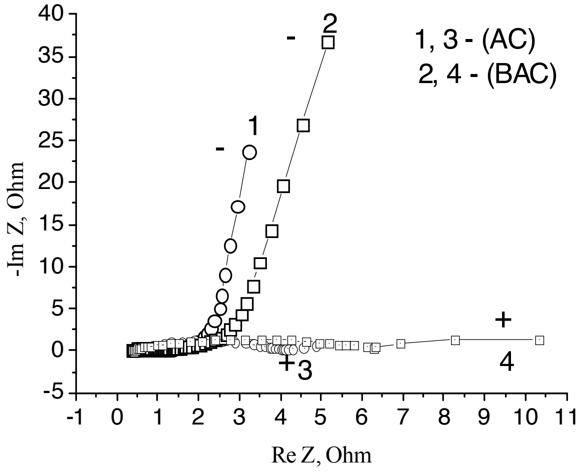

Fig. 5. Nyquist plots for polarization processes in supramolecular complexes C<18-crown-ether-6> in anode 1, 2 and cathode 3, 4 regions

As is shown for both kinds of carbon they are of the same type: in negative region of potentials exist the blocking faraday processes, whereas at positive potentials – transfer of mass/charge through interface. Obviously that processes in negative region, which are typical for capacitive energy storage are the limiting processes. This is well confirmed by "capacitor" behaviour of cyclic voltage- current plot, measured in system with two identical supramolecular electrodes (Fig. 6). At the same time it is the evidence of higher capacitance for system on the base of AC.

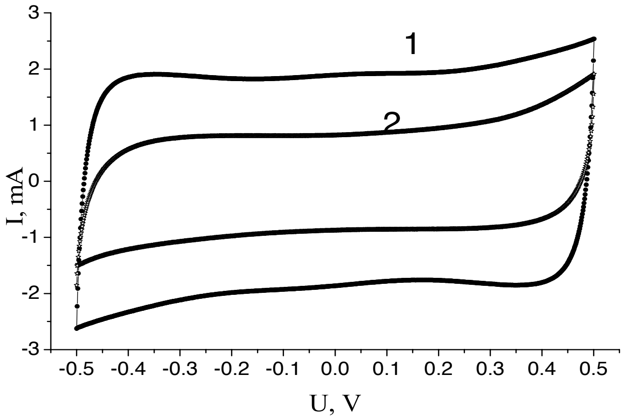

Fig. 6. Cyclic voltage-current plots for supramolecular complexes C<18-crown-ether-6> on the base of AC (1), and BAC (2)

Analysis of frequency dependences of complex impedance Z by means of grapho-analytical method in medium of software ZView 2.3 (Scribner Associates) enabled us to plot the equivalent electric circuits for negative (Fig. 7a) and positive (Figs. 7b, 7c) polarization. Approximation errors were less than 4%.

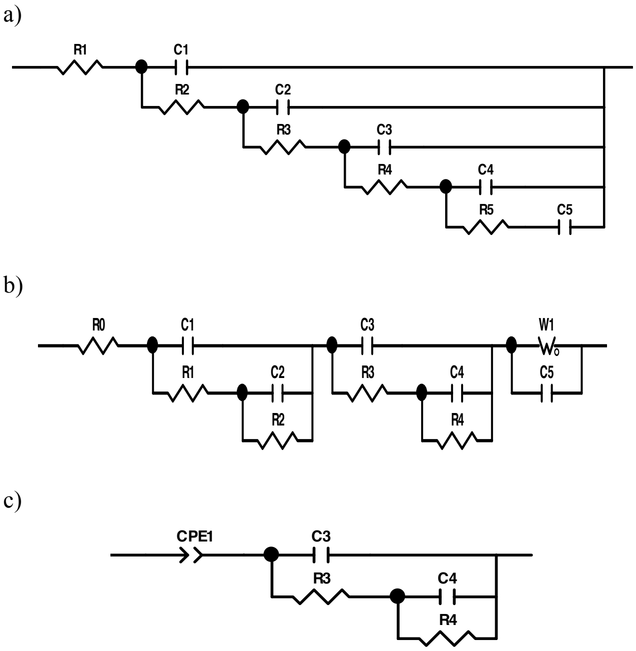

Fig. 7. Equivalent electrical circuits for Nyquist plot of supramolecular complexes C<18-crown-ether-6>

First of them is known as five-unit circuit "Ladder", which corresponds to de Levie model [7], second and third ones depict the faraday heterogeneous current - creating reaction. In order to clarify its effectiveness the following electrochemical system was formed and investigated

-Zn || KOH || C<18-crown-ether-6>+.

Results of galvanostatic cycling for BAC within range of potentials 0-1.24 V and 0.4-1.24 V are shown in Figs. 8 and 9, respectively. Similar curves have been obtained for AC too and are typical for such materials.

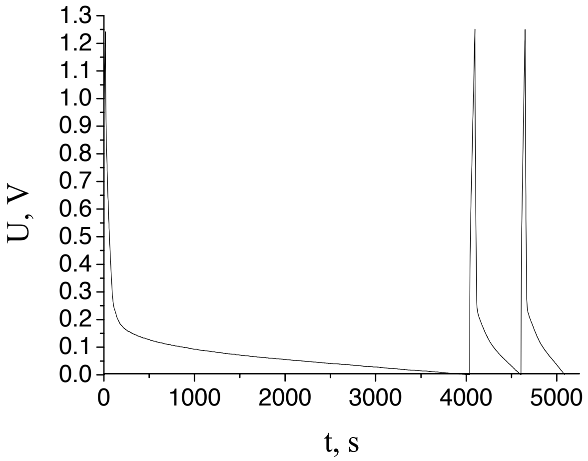

Fig. 8. Cathode–anode galvanostatic cycles for C<18-crown-ether-6> on the base of BAC in potential region 0-1.24 V

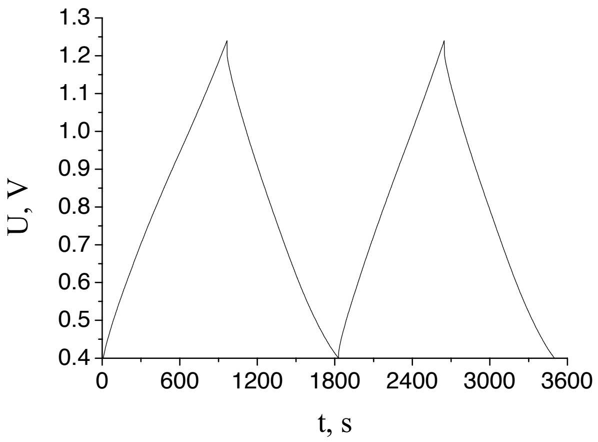

Fig. 9. Cathode-anode galvanostatic cycles for C<18-crown-ether-6> on the base of BAC in potential region 0.4-1.24 V

In 0-0.4 V region the values of specific capacitance for C<18-crown-ether-6> on the base AC equals about ~ 10000 F/g, and in 0.4-1.24 V range – 154 F/g. The same parameters for BAC equal 13350 F/g and 80 F/g, respectively.

This allowed us to note:

- high value of equivalent pseudocapacitance in potential region 0-0.4 V in fact corresponds to arc-like Nyquist plot (Fig. 5) and is related with faraday generation of energy. Behaviour of galvanostatic curves, represented in Fig. 8 is the evidence of such kind energy generation;
- at positive polarization of C<18-crown-ether-6> in range 0.4-1.24 V (that can not be reached in symmetrical cell) capacitance values show the capacitive character of energy storage.

Therefore this system concerning to essence is functional-hybrid with potential regions of faraday generation and non-faradaic energy storage.

4. Conclusions

1. At anode polarization the organic receptor 18-crown-ether-6, introduced in activated carbon, bonds the potassium cations, decreasing in such way the active surface area and as result also the specific capacitance.
2. In positive region of potentials this receptor unblocks it concerning to faraday processes due to bonding with carbon matrix. Processes in negative region of potentials are the limiting ones in symmetrical system with electrodes on the base of C<18-crown-ether-6>.
3. The substitution of negative electrode in last system by zinc one leads to the broadening of polarization region C<18-crown-ether-6> comparatively with symmetrical cell. Therefore, at potentials 0.4–1.24 V the capacitive energy storage is observed, while at lower than 0.4 V potentials the faraday generation of energy.
4. BAC-based supramolecular complex C<18-crown-ether-6> show better results for faraday generation of energy, whereas AC-based one – for capacitive energy storage.
5. Porous structure as well as fractal one of investigated materials are dominant factors at searching of materials for generation, storage and transformation of energy.

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